

AD-A063 915

ILLINOIS UNIV AT URBANA-CHAMPAIGN ROGER ADAMS LAB
INVESTIGATION OF THE MECHANISM OF THE UNIMOLECULAR AND THE ELEC--ETC(U)
JAN 79 6 B SCHUSTER, B 6 DIXON

F/6 7/2

N00014-76-C-0745

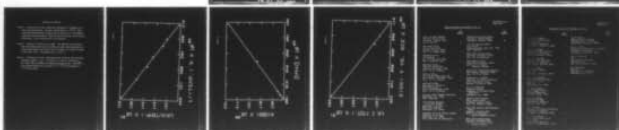
UNCLASSIFIED

NL

| OF |

AD
A063915

1



END

DATE
FILMED

4-79

DDC

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER N0014-76-C-0745-17	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Investigation of the Mechanism of the Unimolecular and the Electron Donor Catalyzed Thermal Fragmentation of Secondary Peroxy Esters. Chemiluminescence of 1-Phenylethyl Peroxyacetate.		5. TYPE OF REPORT & PERIOD COVERED Technical
7. AUTHOR(s) Gary B. Schuster and Brian G. Dixon		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of Illinois Urbana, IL 61801		8. CONTRACT OR GRANT NUMBER(s) N0014-76-C-0745
11. CONTROLLING OFFICE NAME AND ADDRESS Chemistry Program, Materials Science Division, Office of Naval Research, 800 N. Quincy Street, Arlington, VA 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-051-616
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE January 12, 1979
<div style="position: relative; width: 100%; height: 100%;"> <div style="position: absolute; top: 50%; left: 50%; transform: translate(-50%, -50%) rotate(-45deg); font-size: 4em; font-weight: bold; opacity: 0.5;">LEVEL</div> </div>		13. NUMBER OF PAGES 17
		15. SECURITY CLASS. (of this report) Unclassified
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Chemiluminescence Electron Transfer Peroxide Thermolysis		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The mechanism of the thermolysis of 1-phenylethyl peroxyacetate was studied. In the absence of easily oxidized substrates this perester undergoes thermal fragmentation to yield quantitatively acetophenone and acetic acid. These products are formed by initial oxygen-oxygen bond homolysis followed by in cage hydrogen atom transfer. A small fraction of the so formed acetophenone is generated in an electronically excited state. In the presence of easily oxidized substrates the reaction of the perester is catalyzed and generates excited states by the chemically initiated electron-exchange lumi-		

DD FORM 1473
1 JAN 73EDITION OF 1 NOV 65 IS OBSOLETE
GPO 9102-914-6001

Unclassified

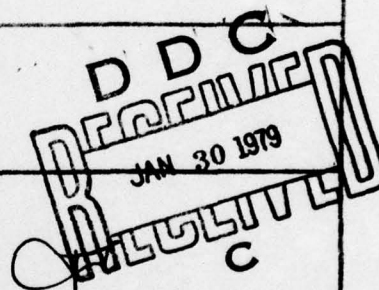
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

(cont.)

79 01 26 060

AD A063915

DDC FILE COPY



20. nescence (CIEEL) mechanism. An analogy with the catalyzed reaction is drawn to the excitation step of bacterio-luminescence.

LONG LIFE COPY

RECEIVED
JAN 30 1970
DDC

79 01 26 000

(15) N0014-76-C-0745

OFFICE OF NAVAL RESEARCH

Contract N0014-76-C-0745

Task No. NR-051-616

(9) TECHNICAL REPORT NO. N0014-76-C-0745-17

(6) Investigation of the Mechanism of the Unimolecular and
The Electron Donor Catalyzed Thermal Fragmentation of Secondary
Peroxy Esters. Chemiluminescence of 1-Phenylethyl Peroxyacetate.

by

(10) Gary B. Schuster ~~and~~ Brian G. Dixon

(12) 17p.

Prepared for Publication

in

Journal of the American Chemical Society

School of Chemical Sciences

University of Illinois

Urbana, Illinois 61801

(11) 12 Jan ~~1976~~ 79

Reproduction in whole or in part is permitted for
any purpose of the United States Government

Approved for Public Release; Distribution Unlimited.

ACCESSION for	
NTIS	White Section <input checked="" type="checkbox"/>
DDC	Black Section <input type="checkbox"/>
UNAVAILABILITY	<input type="checkbox"/>
DISTRIBUTION	
BY	
DISTRIBUTION/AVAILABILITY CODES	
D. SPECIAL	
A	-

409 798

79 01 26 060

Liu

Investigation of the Mechanism of
the Unimolecular and The Electron Donor Catalyzed
Thermal Fragmentation of Secondary Peroxy Esters.
Chemiluminescence of 1-Phenylethyl Peroxyacetate.

Brian G. Dixon and Gary B. Schuster*¹⁷

Department of Chemistry
Roger Adams Laboratory
University of Illinois
Urbana, IL 61801

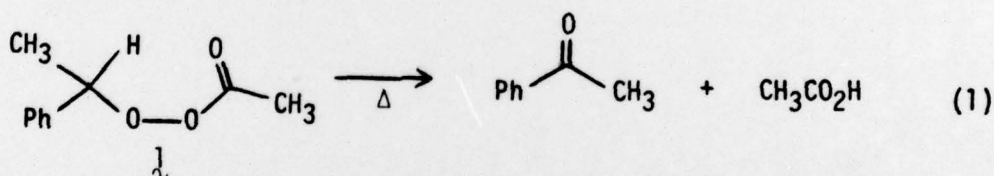
Abstract:

The mechanism of the thermolysis of 1-phenylethyl peroxyacetate was studied. In the absence of easily oxidized substrates this perester undergoes thermal fragmentation to yield quantitatively acetophenone and acetic acid. These products are formed by initial oxygen-oxygen bond homolysis followed by in cage hydrogen atom transfer. A small fraction of the so formed acetophenone is generated in an electronically excited state. In the presence of easily oxidized substrates the reaction of the perester is catalyzed and generates excited states by the chemically initiated electron-exchange luminescence (CIEEL) mechanism. An analogy with the catalyzed reaction is drawn to the excitation step of bacterio-luminescence.

Investigation of the Mechanism of
the Unimolecular and the Electron Donor Catalyzed
Thermal Fragmentation of Secondary Peroxy Esters.
Chemiluminescence of 1-Phenylethyl Peroxyacetate.

Sir:

Our interest in highly exoergic thermal reactions of organic peroxides led us to the investigation of 1-phenylethyl peroxyacetate (**1**). Thermolysis of **1** in benzene solution gives a quantitative yield of acetic acid and acetophenone,¹ a small fraction of which is electronically excited. The reaction of **1** is catalyzed by a wide range of easily oxidized substances. In this case, the electronically excited state of the catalyst (activator) is formed, apparently by the recently described chemically initiated electron-exchange (CIEEL) mechanism.² We report herein our examination of the mechanism of both the unimolecular and catalyzed reaction of **1**.



Perester **1** was prepared by the acid catalyzed reaction of ketene with 1-phenylethylhydroperoxide in CH_2Cl_2 and purified by distillation.³ The thermolysis of **1** in argon purged benzene can be followed conveniently by the indirect or activated⁴ chemiluminescence that results upon addition of biacetyl or any one of several easily oxidized fluorophores (see below) respectively. The rate at which the perester reacted showed apparent first-order kinetic behavior. However, the observed rate constants and derived activation parameters for solutions $1 \times 10^{-2} \text{ M}$ and above are dependent upon the initial perester concentration, indicating the likely involvement of a radical induced homolysis path.⁵ At low

initial perester concentration (1×10^{-5} - 1×10^{-3} M) the rate of reaction is independent of concentration. Moreover, the activation parameters for the reaction, $\Delta H^\ddagger = 33.2 \pm 0.7$ kcal/mole, $\Delta S^\ddagger = 11.0 \pm 1.9$ eu (see Figure 1), under these conditions indicate a unimolecular process.⁶

In contrast to the modified Russell mechanism⁷ suggested by Hiatt and co-workers⁸ for the thermolysis of secondary peresters, our findings are more consistent with a stepwise process in which oxygen-oxygen bond homolysis is followed by rapid in-cage hydrogen atom abstraction. In particular, the activation enthalpy indicates a transition state in which bond cleavage is uncompensated by bond formation.⁶ And the quantitative yield of acetic acid rules out escape from the solvent cage of a significant amount of the so formed acetyloxy radical.⁹ The calculated heat of reaction for the process shown in eq. 1 is -58 kcal/mole.¹⁰ Thus, the transition state for this reaction lies some 94 kcal/mole above ground state products. Sufficient energy is released therefore to populate electronically excited states of acetophenone.¹¹ Indeed, we detect a low yield of excited state product as indirect chemiluminescence from added biacetyl. The emission spectrum of the chemiexcited biacetyl is composed entirely of the phosphorescence, thus implicating acetophenone triplet as its precursor. This mechanism is shown as path A in Scheme I.

When a small amount of an easily oxidized substance is added to benzene solutions of perester **1**, the thermolysis reaction is somewhat different. For example, N,N-dimethyldihydrodibenzo[a,c]phenazine (DMAC)¹² accelerates the rate of reaction of **1** (Figure 2) without itself being consumed. The products of this reaction are acetic acid and acetophenone, formed quantitatively as they were for the uncatalyzed case. Electronically excited states are formed by the catalytic reaction as well, and, in contrast to the unimolecular transformation, are detected as the

fluorescence of the excited singlet state of the activator. The DMAC is not unique in its catalytic ability. Similar observations were made for N,N-diphenyl-2-aminopyrene (DPAP),¹³ zinc tetraphenylporphyrin, rubrene, perylene, 9,10-diphenylethynylanthracene, and others.

The relative catalytic rate constant for the various activators was determined by measuring the total chemiluminescent light intensity under conditions where most of I_2 reacted by the unimolecular path (i.e. low activator concentration). After correcting for differences in fluorescence quantum yield and photomultiplier tube and monochromator spectral efficiency, it is apparent that the only correlation of activator property and rate constant is with the one electron oxidation potential (Table 1 and Figure 3).

These findings are just those that one would expect for a CIEEL process. Electron transfer from the activator to perester I_2 is endothermic but may be made irreversible by rapid cleavage of the oxygen-oxygen bond of the reduced peroxide. The rate of this reaction is expected to depend upon the oxidation potential of the activator. Transfer of a hydrogen atom simultaneously with or subsequent to oxygen-oxygen bond cleavage generates acetophenone radical anion in the same solvent cage as the activator radical cation. Charge annihilation of these radical ion intermediates leads to the observed excited state product. This mechanism is shown as path B in Scheme I for DMAC.

This is the fourth well-documented case of an electron-transfer initiated reaction of a peroxide that leads to electronically excited state product.² As in the previously described examples, the major evidence is the correlation of rate constant and oxidation potential, i.e. Figure 3. Comparisons among the various peroxides reveal that the catalytic rate constant is strongly dependent upon structure--diacylperoxides react much more rapidly than

peresters, which are more difficultly reduced, for example.¹⁴ However, the magnitude of the slope of the line resulting from the semilog plot of rate against activator oxidation potential is essentially constant and equal to ca. $-0.3/RT$ for the systems investigated to date. This result is consistent with rate limiting irreversible electron transfer from activator to peroxide occurring with a transfer coefficient of ca. 0.3.¹⁵

In summary, we have observed two distinct reaction paths for thermolysis of secondary perester λ . The unimolecular reaction appears to proceed by a step-wise route, the bimolecular reaction with electron donors by an electron transfer mechanism. The electron transfer mechanism in particular may serve as a model for the excitation step in the bacterioluminescence reaction.¹⁶ We are continuing our investigation of this and other aspects of the chemistry of these peresters.

Acknowledgment. We would like to thank Professor Faulkner of this department for many helpful discussions. The authors gratefully acknowledge financial support for this work by the Office of Naval Research, The National Science Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We would also like to thank Mr. Steven P. Schmidt for preparing and purifying the DMAC and DPAP.

Brian G. Dixon and Gary B. Schuster*¹⁷

Department of Chemistry
Roger Adams Laboratory
University of Illinois
Urbana, IL 61801

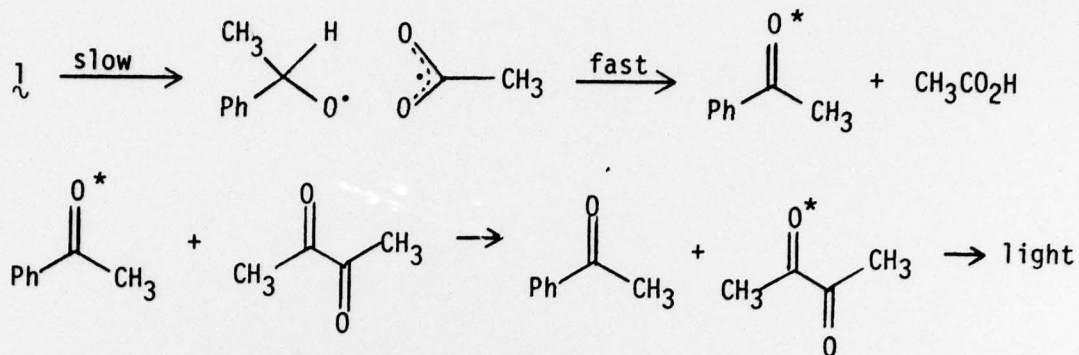
References and Notes

- 1) The products were identified by comparison with authentic material. The yield of acetic acid was determined by gas chromatography on a Poropak Q column at 245°C; the yield of acetophenone by gas chromatography on a 3% SE-30 on Chromasorb Q column at 100°C.
- 2) J.-y. Koo and G. B. Schuster, J. Am. Chem. Soc., **100**, 4496 (1978); S. P. Schmidt and G. B. Schuster, ibid., **100**, 1966 (1978); J. P. Smith and G. B. Schuster, ibid., **100**, 2564 (1978); J.-y. Koo and G. B. Schuster, ibid., **99**, 6107 (1977).
- 3) Peroxy ester **1** was characterized as follows: IR(CCl₄) 3000, 1785, 1500, 1285 cm⁻¹. ¹Hnmr (CCl₄ internal TMS) δ 1.50(d, 3H, J = 7 Hz), δ 1.9 (s, 3H), δ 5.17 (q, 1H, J = 7 Hz), δ 7.3 (s, 5H) Analysis: Calcd. for C₁₀H₁₂O₃; C, 66.64; H, 6.73; Found; C, 66.98; H, 6.66. In addition perester **1** was reduced with triethyl phosphite to 1-phenyl ethyl acetate which was characterized by comparison with authentic material.
- 4) We propose the following definitions:
 - i) Direct chemiluminescence - The emission of light is from the excited state formed as a direct result of a unimolecular thermal chemical reaction.
 - ii) Indirect chemiluminescence - The emission of light is from an excited state formed as a result of energy transfer from the initially generated excited state.
 - iii) Activated chemiluminescence - The emission of light is from an excited state directly formed from a bimolecular reaction between substrate and catalyst.
- 5) R. A. Wolf, M. J. Migliore, P. H. Fuery, P. R. Gagnier, I. C. Sabeta, and R. J. Trocino, J. Am. Chem. Soc., **100**, 7967 (1978); K. Nozaki and P. D. Bartlett, J. Am. Chem. Soc., **68**, 1686 (1946).

- 6) W. A. Pryor and K. Smith, Int. J. Chem. Kinet., 3, 387 (1971); P. D. Bartlett and R. R. Hiatt, J. Am. Chem. Soc., 80, 1398 (1958); J. P. Lorand and P. D. Bartlett, ibid., 88, 3294 (1966).
- 7) G. A. Russell, J. Am. Chem. Soc., 79, 3871 (1957).
- 8) R. R. Hiatt, L. C. Glover, and H. S. Mosher, J. Am. Chem. Soc., 97, 1556 (1975).
- 9) J. C. Martin, J. W. Taylor, and E. H. Drew, J. Am. Chem. Soc., 89, 129 (1967) and references cited therein.
- 10) S. Benson, "Thermochemical Kinetics", 2nd Ed., Wiley, New York, NY, 1976.
- 11) E. B. Wilson, J. Am. Chem. Soc., 98, 3387 (1976); E. Lissi, ibid., 98, 3386 (1976).
- 12) J. G. Smith and E. M. Levi, J. Organomet. Chem., 36, 215 (1972).
- 13) Prepared by reaction of 1-aminopyrene with bromo benzene and lithium tetramethyl piperidide in THF. Analysis: Calcd. for $C_{28}H_{19}N$; C, 91.02; H, 5.18; N, 3.79; Found; C, 90.77; H, 4.99; N, 3.78.
- 14) For the series diphenoyl peroxide, dimethyldioxetanone, perester 1 we estimate that k_{cat} for DMAC is ca. 7×10^3 , 240, $0.1 \text{ M}^{-1}\text{s}^{-1}$, respectively.
- 15) P. Delahay, "Double Layer and Electrode Kinetics", Wiley-Interscience, New York, NY, 1965, chapter 7.
- 16) J. W. Hastings and K. H. Nealson, Ann. Rev. Microbiol., 31, 549 (1977).
- 17) Fellow of the Alfred P. Sloan Foundation, 1977-79.

Scheme I

Path A - Indirect Chemiluminescence



Path B - Activated Chemiluminescence.

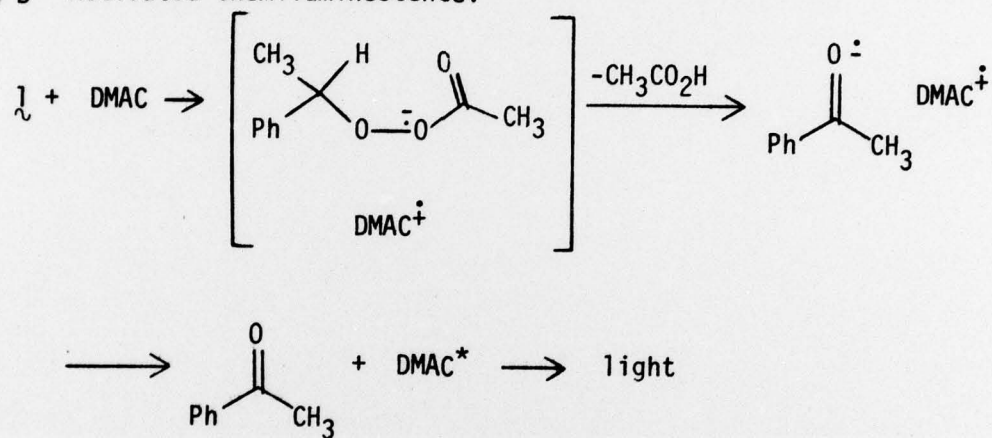


Table 1.

Activator	E_s^a (kcal/mole)	E_{ox}^b (V vs. SCE)	ϕ_{fl}^c	k_{cat}^d ($M^{-1}s^{-1}$)
Perylene	65	1.00	0.84	1.19×10^{-4}
Rubrene	54	0.82	0.56	$1.40 \times 10^{-4}^e$
Diphenylethynyl- anthracene	62	1.16	0.96	3.58×10^{-5}
DPAP	68	0.90	1.00	2.35×10^{-4}
DMAC	58	0.25	0.04	9.73×10^{-2}

- a. Assigned from the 0-0 band of the fluorescence spectrum.
- b. Determined by cyclic voltometry in CH_3CN solution with tetrabutylammonium perchlorate supporting electrolyte.
- c. At 90° in argon saturated benzene solution.
- d. Calculated by comparing relative total intensity to that of DMAC.
- e. Self absorption by rubrene may lead to the observed low calculated value for k_{cat} .

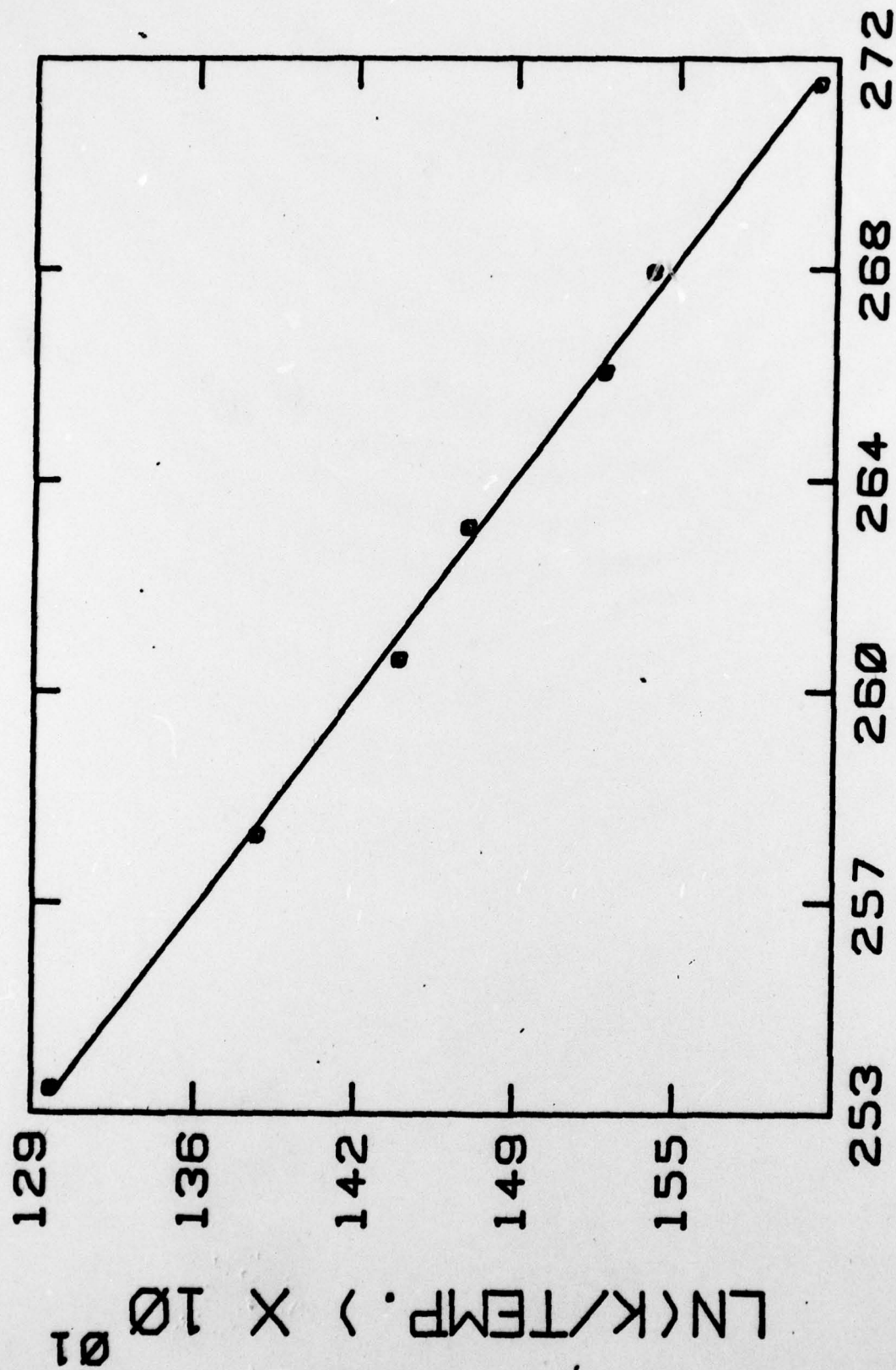
Captions for figures

Figure 1. Eyring plot for the unimolecular thermolysis of perester λ in argon saturated benzene. Perester concentration 3×10^{-4} M. Rate constants were determined by measuring the decrease in 9,10-diphenylanthracene chemiluminescence intensity which was shown to be directly proportional to the concentration of the perester.

Figure 2. Catalysis of perester λ by DMAC. The observed rate constants were determined by monitoring the DMAC activated chemiluminescence in argon purged benzene solution at 99.9° and were first order for three or more half-lives. The perester was 3×10^{-4} M.

Figure 3. Correlation of total chemiluminescence intensity with activator oxidation potential (E_{ox}). The points, in order of increasing E_{ox} are: DMAC, DPAP, perylene and diphenylethynylanthracene. Measured in argon purged benzene with activator at 1×10^{-4} M and perester at 1×10^{-3} M at 99.5° .

Figure 1.



$1/(TEMP. \times 10^5)$

Figure 2.

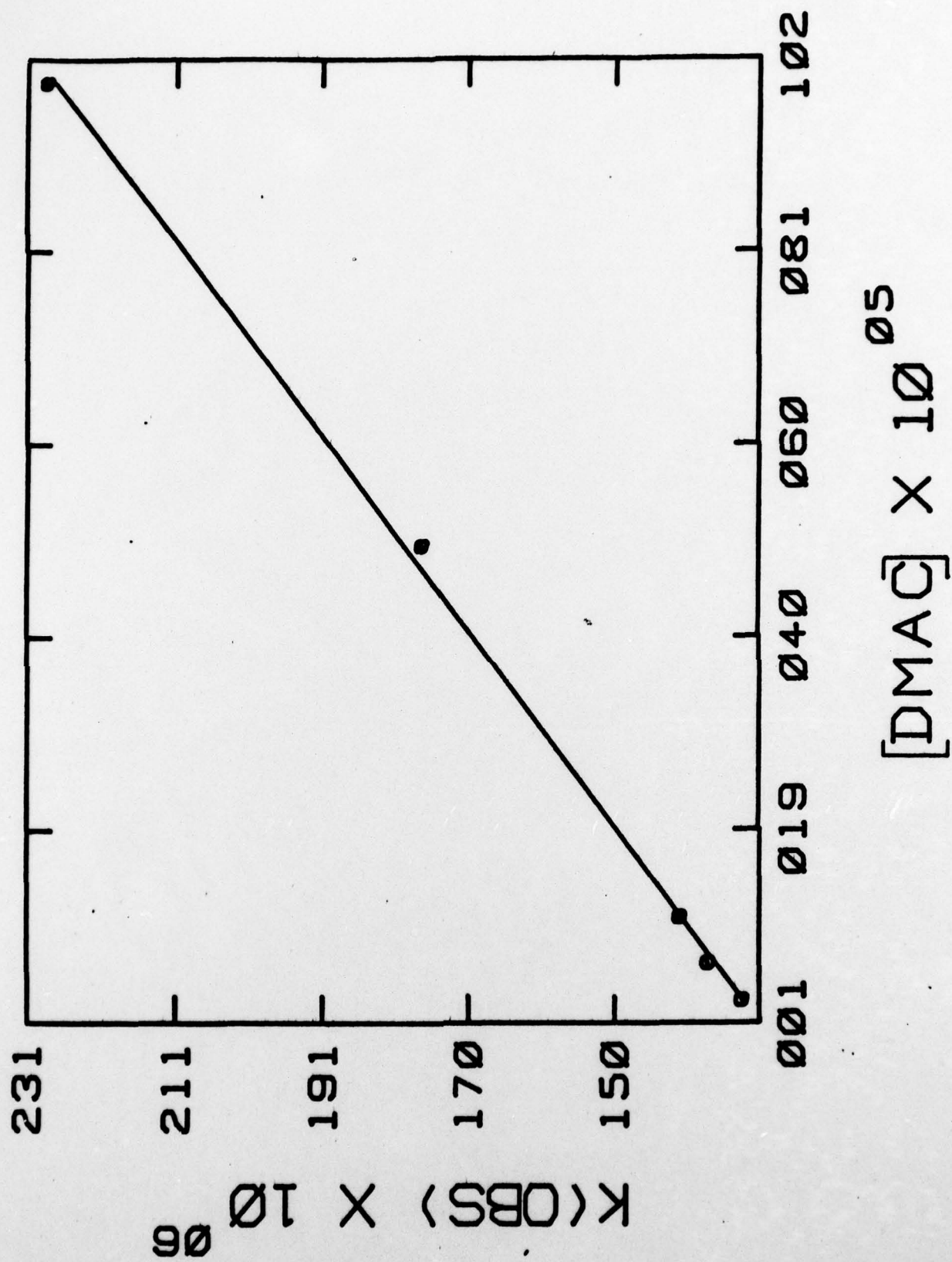
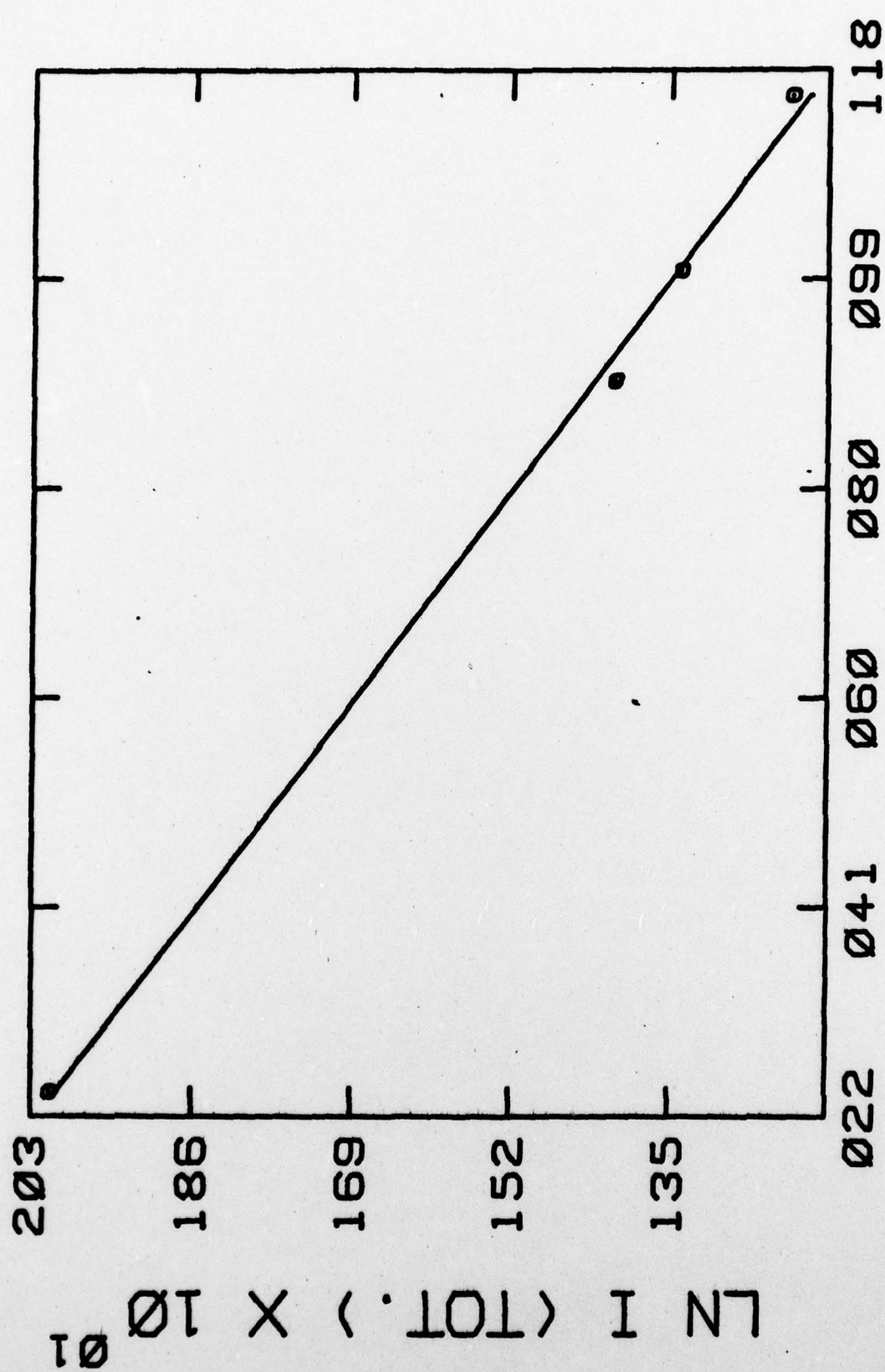


Figure 3.



E(OX) V VS. SCE X 10²

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research 800 North Quincy Street Arlington, Virginia 22217 Attn: Code 472	2	Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12
ONR Branch Office 536 S. Clark Street Chicago, Illinois 60605 Attn: Dr. George Sandoz	1	U.S. Army Research Office P.O. Box 1211 Research Triangle Park, N.C. 27709 Attn: CRD-AA-IP	1
ONR Branch Office 715 Broadway New York, New York 10003 Attn: Scientific Dept.	1	Naval Ocean Systems Center San Diego, California 92152 Attn: Mr. Joe McCartney	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106 Attn: Dr. R. J. Marcus	1	Naval Weapons Center China Lake, California 93555 Attn: Dr. A. B. Amster Chemistry Division	1
ONR Area Office One Hurlidie Plaza, Suite 601 San Francisco, California 94102 Attn: Dr. P. A. Miller	1	Naval Civil Engineering Laboratory Port Hueneme, California 93401 Attn: Dr. R. W. Drisko	1
ONR Branch Office Building 114, Section D 666 Summer Street Boston, Massachusetts 02210 Attn: Dr. L. H. Peebles	1	Professor K. E. Woehler Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Director, Naval Research Laboratory Washington, D.C. 20390 Attn: Code 6100	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
The Assistant Secretary of the Navy (R,E&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Office of Naval Research 800 N. Quincy Street Arlington, Virginia 22217 Attn: Dr. Richard S. Miller	1
Commander, Naval Air Systems Command Department of the Navy Washington, D.C. 20360 Attn: Code 310C (H. Rosenwasser)	1	Naval Ship Research and Development Center Annapolis, Maryland 21401 Attn: Dr. G. Bosmajian Applied Chemistry Division	1
		Naval Ocean Systems Center San Diego, California 91232 Attn: Dr. S. Yamamoto, Marine Sciences Division	1

TECHNICAL REPORT DISTRIBUTION LIST, 051A

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. M. A. El-Sayed University of California, Los Angeles Department of Chemistry Los Angeles, California 90024	1	Dr. M. Rauhut American Cyanamid Company Chemical Research Division Bound Brook, New Jersey 08805	1
Dr. M. W. Windsor Washington State University Department of Chemistry Pullman, Washington 99163	1	Dr. J. I. Zink University of California, Los Angeles Department of Chemistry Los Angeles, California 90024	1
Dr. E. R. Bernstein Colorado State University Department of Chemistry Fort Collins, Colorado 80521	1	Dr. B. Schechtman IBM San Jose Research Center 5600 Cottle Road San Jose, California 95143	1
Dr. C. A. Heller Naval Weapons Center Code 6059 China Lake, California 93555	1	Dr. John Cooper Code 6130 Naval Research Laboratory Washington, D.C. 20375	1
Dr. J. R. MacDonald Naval Research Laboratory Chemistry Division Code 6110 Washington, D.C. 20375	1		
Dr. G. B. Schuster University of Illinois Chemistry Department Urbana, Illinois 61801	1		
Dr. E. M. Eyring University of Utah Department of Chemistry Salt Lake City, Utah	1		
Dr. A. Adamson University of Southern California Department of Chemistry Los Angeles, California 90007	1		
Dr. M. S. Wrighton Massachusetts Institute of Technology Department of Chemistry Cambridge, Massachusetts 02139	1		